

Water Quality
Lesson 4
Carlsbad Environment Monitoring and Research Center

Analysis of Metals and Trace Elements Procedures

Learner Outcomes

The learner will

- Properly prepare containers for water collection.
- Collect water samples using extreme caution to eliminate contamination of samples that contain metals and trace elements.
- Conduct appropriate tests at the study site area.
- Transport, acidify and store samples using standard procedures, until the actual analysis is performed within the required time frame.
- Qualifying students will work side by side with a professional chemist to do a water analysis that is on the cutting edge of instrumental methods for analysis.
- Verify that the procedures used are the latest available methodology revision by checking the Environmental Chemistry Laboratory Procedure Manual Table of Contents for revision number and date.
- Work with personnel from the Carlsbad Environmental Monitoring and Research Center to test the samples by Inductively-Coupled Plasma Emission Spectroscopy (ICP-ES) and Atomic Absorption Spectroscopy (AA).
- Record all pertinent information regarding this activity into their Chihuahuan Desert Lab notebooks using acceptable methods of notation for future reference.

Background

The following procedures have been modified to meet the cave water testing criteria for the Chihuahuan Desert Lab from the Standard Operating Procedures EC SOP-009 and EC SOP-004 Revision 2.0 modified on July 15, 1998, written by the Environmental Chemistry Laboratory at the Carlsbad Environmental Monitoring and Research Center in Carlsbad, New Mexico.

This procedure is applicable for the determination of metals by using Inductively-Coupled Plasma Emission Spectroscopy (ICP-ES) and Atomic Absorption Spectroscopy (AA) on drinking water and surface waters (cave pond water). The analytical instrumentation can be used to determine the dissolved analytes in aqueous samples after filtration and acid preservation, and total recoverable metals after an evaporation/acid-digestion procedure.

An aliquot of well mixed, homogenous, aqueous sample is accurately weighed or measured for sample processing. For dissolved analysis of aqueous samples, the sample is analyzed directly by the instrument after filtration and acid matrix matching. For total recoverable analysis, aqueous samples are treated with nitric and hydrochloric acid before analysis.

As with all trace analysis applications, extreme caution must be used to eliminate any chance of sample contamination with metals and trace elements. Labware should be acid cleaned and dried in a trace metal-free clean bench. Sampling containers should be cleaned and stored in sealable plastic bags. The utmost care should be exercised during the sample preparation.

Students and laboratory personnel should verify that this procedure is the latest available revision by checking the Environmental Chemistry Laboratory Procedure Manual Table of Contents for revision number and date. The latest revision of this document shall be in the environmental chemistry laboratory at all times. Personnel should be familiar with the MSDS (available in the lab and from the Chemical Hygiene Officer, CHO) for each chemical used in this procedure. Proper personal protective equipment (gloves, lab coat, eye protection) shall be worn while performing this procedure. Operations that might generate fumes must be performed in a fume hood.

Background for Procedures

- Only students 18 or older may perform procedures at the Carlsbad Environmental Monitoring and Research Center.
- Prior to the collection of an aqueous sample, consideration should be given to the type of data required (i.e., dissolved or total recoverable) so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing, or before "direct analysis," to ensure the sample has been properly preserved. If properly preserved with acid, samples can be held up to six months before analysis.
- For the determination of the dissolved elements, the sample must be filtered through a 0.45 micrometer pore diameter membrane filter at the time of collection or as soon thereafter as possible. (The use of plastic filtering apparatus is recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use the first ~10mL portion of the filtered sample to rinse the filter flask, discard this portion and collect the filtrate (the volume will not be critical, just collect enough for the analyses that are planned). Immediately following filtration, acidify the filtrate with nitric acid and hydrochloric acid to pH<2.
- For the determination of total recoverable elements in aqueous samples, the samples are not filtered, but acidified with nitric and hydrochloric acid to pH<2. Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions and possible contamination, it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH<2 just prior to withdrawing an aliquot for processing or "direct" analysis. If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for sixteen hours until verified to pH<2.

Caution: When the nature of the sample is either unknown or is known to be hazardous, acidification should be performed in a fume hood.

- For aqueous samples, a field blank should be prepared and analyzed, as required by the data user. Use the same type of container and acid as used in sample collection.
- The ICP internal standard used in this method is added in the same concentration to the calibration standards, calibration check standards, and samples. Therefore, no dilution factor is calculated, because all standards and samples have been diluted by the same amount.
- For quality assurance, laboratory notebooks will be maintained and periodically reviewed by the laboratory supervisor.

Materials (Apparatus/Instruments, Reagents, Forms)

- Supplement numbers 5.17, 5.18
- Volumetric flasks, Class A, variety of sizes
- Pipettes, calibrated, with pre-cleaned disposable tips, variety of volumes
- 50mL and 15mL pre-cleaned centrifuge cones
- Water purification apparatus
- Analytical balance
- Ion chromatography syringe filters, 0.45 micron
- 10mL syringes with Luer-Lok® fittings
- Electric hot plates
- Pre-cleaned glass beakers
- Pre-cleaned watch glasses
- Whatman 41 filter paper
- Pre-cleaned filter funnels
- Graduated cylinders
- Ultrapure water
(Deionized water with a specific resistance of 17.8 megaohm-cm or greater, free of ionized impurities, organics, microorganisms and particulate matter larger than 0.2mm. Available from the Barnstead® system located in the Environmental Chemistry Laboratory.)
- Nitric acid (concentrated, high purity)
- Nitric acid 50% (Add 50mL concentrated acid to 50mL ultrapure water in a suitable container, mix thoroughly.)
- Hydrochloric acid (concentrated, high purity)
- Hydrochloric acid 50% (Add 50mL concentrated acid to 50mL ultrapure water in a suitable container, mix thoroughly.)
- Hydrofluoric acid (concentrated, high purity)
- Boric acid (high purity crystals)
- Boric acid, saturated solution (Place equal amounts of boric acid crystals and ultrapure water in a suitable container and mix well. All of the boric acid will not go into solution. When the aqueous layer has been exhausted, add more ultrapure water and mix well.)
- Yttrium standard (1000ppm, purchase prepared, traceable to NIST)

- 100ppm Yttrium internal standard solution (To a volumetric flask containing approximately 10mL ultrapure water and 2mL high purity nitric acid, accurately measure 10mL 1000ppm Yttrium standard. Dilute to volume with ultrapure water.)
- ICP/AA spiking solution -- pipette 5mL of each of the following solutions:
 - Ultra Scientific CLP ICP Spike Standard #1
 - Ultra Scientific CLP ICP Spike Standard #2
 - Ultra Scientific CLP ICP Spike Standard #3(Into a 100mL volumetric flask, add 1mL concentrated nitric acid and dilute to 100 mL with ultrapure water. Use 1mL of this spiking solution for matrix spike samples, diluted to 50mL).
- Laboratory personnel will sign and obtain a copy of the CEMRC Sample Chain of Custody.
- Students will record all observations, procedures and methods in their Chihuahuan Desert Lab notebooks under a section they label as Sample Prep logbook.

Assessments

- Performance in Testing Metals (feed-back from scientists working with students)

Activity #1

Aqueous-Dissolved Analytes

Procedure

- Sample Preparation: Pour an aliquot of sample in a labeled, trace metal-free, 50mL centrifuge cone. Draw 10mL of the sample into a 10mL syringe and attach a 0.45 micron syringe filter to the fitting on the end of the syringe. Push in the plunger and discard the filtered sample. Remove the syringe filter and draw another 10mL aliquot of the sample into the syringe. Replace the syringe filter and push in the plunger, emptying the filtered sample into a 15mL labeled, trace metal-free centrifuge cone. Add 50 μ L of concentrated, ultrapure nitric acid and 50 μ L of concentrated, ultrapure hydrochloric acid.
- Prepare a laboratory reagent blank (LRB) for each batch of 10 samples using ultrapure water and preparing it in the same way as the samples
- Prepare a laboratory fortified blank (LFB) for each batch of 10 samples by adding 1 mL of the ICP/AA spiking solution to a 50mL centrifuge cone and diluting to 50mL with ultrapure water. Filter and acidify the LFB in the same way as the samples.
- Prepare a laboratory matrix spike (LMS) by adding 1mL of the ICP/AA spiking solution to 50mL of one sample in a 50mL centrifuge cone. Filter and acidify the LMS exactly like the unspiked samples.
- A duplicate of one sample should be prepared for each batch of ten samples.

Activity #2

Aqueous-Total Recoverable Analytes

Procedure

- Accurately measure 100mL of sample in an appropriate container and place the sample aliquot in an acid-cleaned 250mL beaker. Add 1mL 50% nitric acid and 1mL 50% hydrochloric acid to each sample. Swirl the sample, cover with an elevated

watch glass and place on a hot plate. Heat the samples to incipient boiling, approximately 85°C, and reduce to 20mL.

- Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. **DO NOT BOIL.**
- Transfer each sample into a 50mL trace metal free centrifuge cone with ultrapure water and dilute to 50mL. Allow the sample to settle overnight or centrifuge. If the sample still contains suspended solids, filtration may be required.
- The LRB should be prepared in the same way as the samples using ultrapure water.
- Prepare the LFB from ultrapure water to which 1mL of the ICP/AA spiking solution has been added.
- For the LFM, measure 100mL of a duplicate sample, add 1mL of ICP/AA spiking solution and prepare as outlined above.
- A duplicate of one sample should be prepared for each batch of ten samples.
Do not add more than 10mL 30% peroxide.
- Add 5mL concentrated hydrochloric acid and 10mL water to each sample. Return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling dilute to 100mL in a graduated cylinder or volumetric flask with ultrapure water. After dilution, filter immediately through a Whatman 41 filter paper. The diluted sample has an approximate acid concentration of 5.0% (v/v) nitric/hydrochloric acid.

Activity #3
ICP Analysis

Procedure

- Transfer 10mL of the prepared sample, LRB, LFB, LMS, or duplicate to a 15ml trace metal free centrifuge cone. Add 0.1mL 100ppm Yttrium internal standard to each, analyze using procedure CEMRC ECSOP-004.

Activity #4
AA Analysis

Procedure

- For Hg, the analysis of filters follows the preparation procedure outlined in CEMRC SOPEC-005 or CEMRC SOPEC-010.

Activity #5
Performance Testing for Quality Control

Procedure

- LRBs, LFBs, Duplicates and LFMs result in a 10% quality control check for each batch of samples.

Activity #6
Reproducibility Testing for Quality Control

Procedure

- Analyze a duplicate sample with each sample batch to test reproducibility.

Activity #7
Inputting Data

Procedure

- Input all heavy metal test data into spreadsheet.